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# Updates Regarding an Adsorption, Coalescence & Desorption Technology for De-Oiling Produced Water

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## 1 ABSTRACT

Upstream producers are becoming more aware of the oil concentrations found in the produced water discharged overboard or reinjected into a disposal well or for enhanced oil recovery. This paper will review the operating principles of the process and provide updates on the performance of the Technology developed by the company. Solutions adopted to address produced waters with very tight reverse emulsions will be discussed using case histories from the Middle East and other parts of the world.

## 2 INTRODUCTION

As oil fields mature, the production of water can significantly increase. The industry perceives this excess produced water as a necessary evil that is often a liability and major cost centre. Offshore platforms are faced with additional challenges. The regulations for oil concentration in produced water discharged overboard commonly vary from 29 to 40 ppm. As the water cut increases, the retention time of existing primary separation equipment is reduced to cope with the excess produced water. Failure to handle the water quickly results in the water treatment becoming the bottleneck of the facility. Reduced retention time in the separation equipment can result in difficulties de-oiling the produced water to within discharge regulations.

## 3 OIL/WATER SEPARATION THEORY

The separation of oil from water and the design of oil/water separation equipment are governed by Stokes' Law which states:

$$V_r = gd^2 (\rho_w - \rho_o) / 18\ \eta \tag{1}$$

Where:

| | | |
|---|---|---|
| $v_r$ | = | the oil droplet rise velocity (m/sec) |
| $g$ | = | the g-force applied (m/sec$^2$) |
| $d$ | = | the oil droplet diameter (m) |
| $\rho_w$ | = | the water density (kg/m$^3$) |
| $\rho_o$ | = | the oil density (kg/m$^3$) |
| $\eta$ | = | the water viscosity (kg/m,sec) |

From Stokes' Law, several parameters can be manipulated to augment the separation efficiency of oil from water. However, the single most important parameter that predicts the efficiency of the separation process is the diameter of the oil droplet. The manipulation of the oil droplet diameter will have the largest impact on the rise velocity and separation efficiency. Other issues also play an important role in the separation efficiency process.

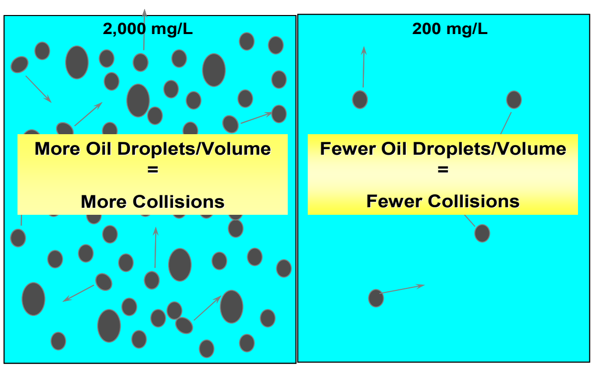


Fig. 1 – Quantity of Oil Droplets per Volume

One characteristic of the produced water that affects separation efficiency is the number of oil droplets found in a unit volume of produced water. Figure 1 shows the population of oil droplets for a sample of produced water with a crude oil concentration of 2,000 mg/L vs. a sample at 200 mg/L. It is clear that the greater the number of oil droplets per unit volume, the greater the probability of two oil droplets colliding and forming a larger oil droplet. The larger oil droplets resulting from collision have a higher rise velocity and thus have a greater chance of separating from the produced water.

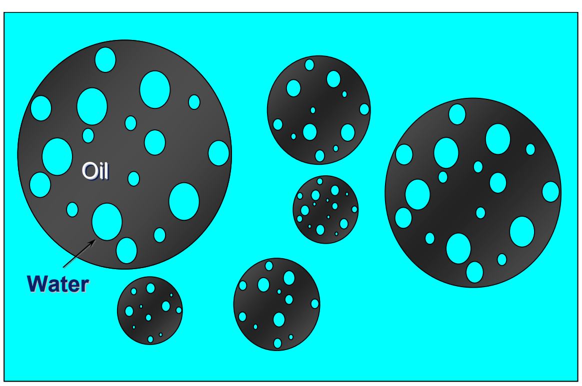


Fig. 2 – Complex Reverse Emulsions

Complex reverse emulsions as shown in Figure 2, can exist and are relatively stable in nature. While these droplets have the ability to collide and form larger droplets and increase the rise velocity, the water contained within the oil droplet remains. Separating the water from within the complex oil droplet often requires the addition of chemicals. Compounding the issue is the need for an efficient distribution of the chemical into the process stream so that maximum contact with the reverse emulsion can take place in order to destabilize the droplets and separate the entrained water.

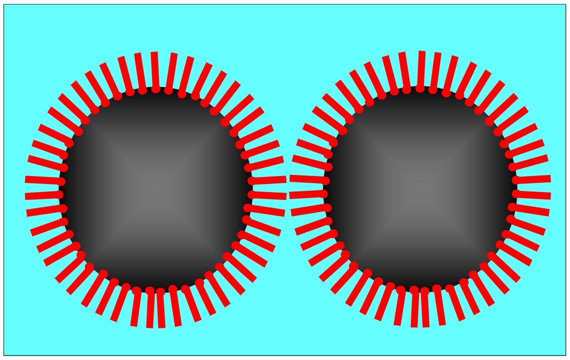

Fig. 3 – Surfactant Coated Oil Droplets

Typical upstream oil and gas processing systems use corrosion inhibitors, polymers, scale inhibitors, de-foamers, biocides and demulsifiers. Some of these chemicals coat the oil droplet and prevent coalescence with other similar oil droplets. This results in a very stable reverse emulsion that is difficult to break. Stokes' Law states that augmenting the diameter of the oil droplet has the greatest single effect on the rise velocity and thus the efficiency of the oil/water separation process. The above mentioned characteristics will add to the difficulty of coalescing small oil droplets to larger ones. When selecting the proper oil/water separation (OWS) equipment, it is paramount to understand the nature of the oil droplets, the size of the droplets in the produced water and their distribution in relationship to their size.

A recent site test using the Jorin ViPA clearly exemplifies the effects that production chemicals have on the de-oiling process of produced water. A gas platform in Southeast Asia produced 500 to 550 MMscf/day of gas at a trunk line pressure of approximately 90 barg and 1,000 to 2,000 BPD of condensates. Produced water volumes from this facility also ranged from 1,000 to 2,000 BWPD. The gas wells are sent to a production separator with the produced water then being funnelled to a parallel plate coalescer (PPC) and finally a skimmer before overboard discharge. Local regulations require the PW to be de-oiled to a level of 30 ppm or less. A corrosion inhibitor (CI) is injected into the process stream at a concentration of 0.1L/MMscf.

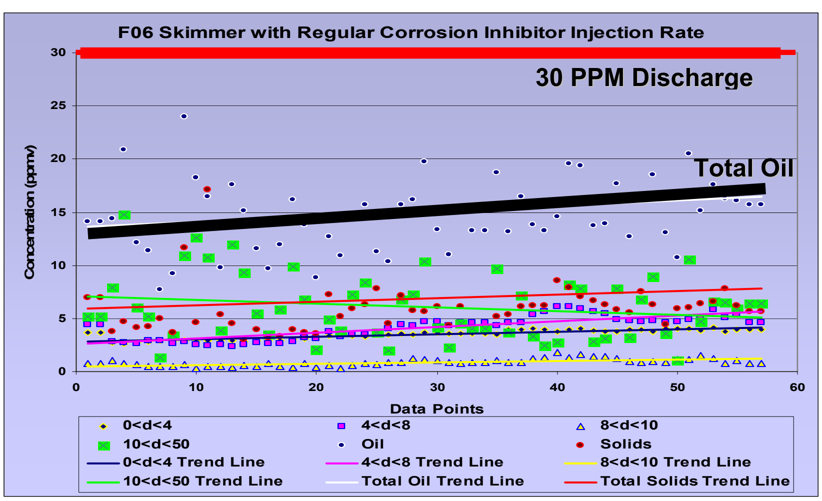


Fig. 4 – ViPA Analysis with Regular CI Injection Rates

Under the above conditions, the PW discharged overboard meets and exceeds the local regulations of 30 ppm. The Jorin ViPA was used to measure a size distribution curve of the treated water. The ViPA was commissioned to calculate concentrations of oil droplet ranges from 0 to 4, 4 to 8, 8 to 10 and 10 to 50 microns. Fig. 4 shows the trend lines of the measurements taken when normal corrosion inhibitor is injected. The solid red line is the discharge OIW target of 30 ppm. The solid black line is the total oil calculated at the discharge from the skimmer. The mean concentration of “Total Oil” was calculated to be ~15 ppm. Under normal conditions, the existing de-oiling equipment consisting of the PPC and skimmer is sufficient to de-oil the PW to well below the discharge regulations of 30 ppm.

The corrosion inhibitor was increased to 0.2L/MMscf and the ViPA was commissioned to measure the same oil droplet ranges. Fig. 5 shows the effect of added CI on the oily water distribution curve. Notice that the “Total Oil Concentration” trend line (in black) has now greatly exceeded the 30 ppm discharge level and the mean concentration value is now ~98 ppm OIW after the skimmer. In this case, the concentration of CI injected has a direct relationship to the oil droplet distribution curve and the ability of the existing de-oiling equipment to meet the current discharge regulations. The results highlight the need to take notice on how the use of common chemicals, their concentrations and perhaps their combinations affect other aspects of the process and in this case the ability of the existing OWS equipment to meet the required overboard discharge regulations.

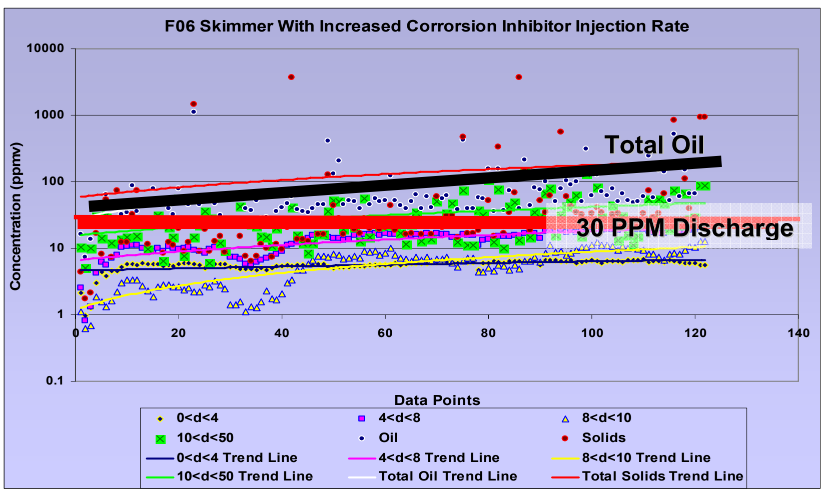

Fig. 5 – ViPA Analysis with Increased CI Injection Rates

## 4 THE TECHNOLOGY – HOW IT WORKS

### 4.1 Technology Overview

The Technology is a multi-stage separation system having the capacity of multi-phase separation of large and small oil droplets (free-floating and dispersed) present in produced water. (See Fig. 6) This is done by means of an adsorbent media, the Reusable Petroleum Adsorbent (RPA®, the media). This material is a polymer-based, oleophilic, hydrophobic, non-toxic, media coalescing agent. [1]

The Technology's separation process consists of routing the oily water to its inlet. The oily water passes through the first vessel containing continuous coalescing elements which contain the media and a recovery chamber. The media continuously adsorbs the dispersed oil, coalesces the smaller droplets and desorbs larger oil droplets. These droplets rise to the top of the vessel's recovery chamber. The oil and remaining solution gas (if any) are retrieved for re-use. The effluent water from the Technology is treated to the customer's requirements then disposed of either overboard as in the case for offshore facilities or re-injected into disposal wells or for enhanced oil recovery. A second vessel stage is available if required. [2]

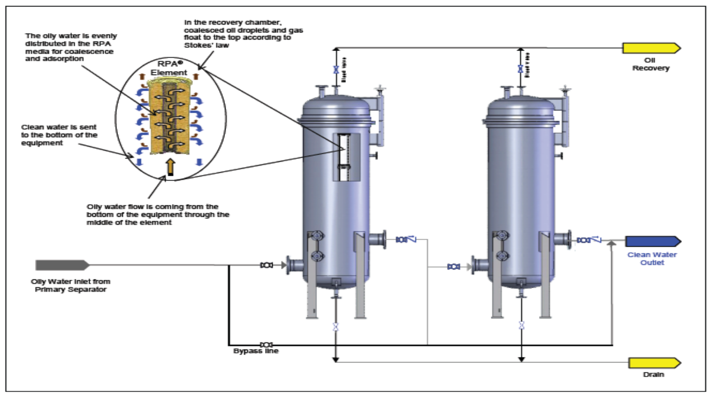

Fig. 6 – General Layout of the Technology

Although upstream oil and gas production and produced water characteristics can vary from one operation to the other, the Technology has reached a stage where it is developed and tested to operate within the following parameters:

- Oil Densities: API° 16 and above.
- Fluid Temperature: up to 95 °C
- Inlet Oil concentrations up to 2000 mg/L
- Oil droplet diameters down to 2 µm
- Flow rates up to 120,000 BWPD with one vessel
- Flow turndown ratio 100:1
- Handles upset conditions

Depending on the characteristics of the produced water to be treated, the efficiency of the system can be enhanced by providing optimized solutions on a case-by-case basis. This implies optimizing the two basic principles behind the Technology being oil coalescence and gravity separation.

### 4.2 Coalescing Element Overview

The coalescing element contains the proprietary media manufactured by the company. The element's dimensions are standard for all sized and models available. The element is approximately 20 inches high, 6 inches outside diameter and 2 inches inner core. The number of elements contained in one vessel increases to accommodate the produced water flow rates.

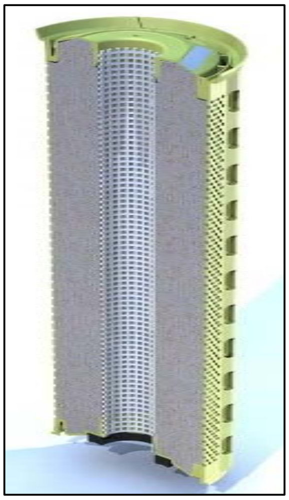

Fig. 7 – Cutaway of Coalescing Element

Three variables within the element can be modified to provide efficient coalescing properties to suit the specific site conditions. Permeability can be altered by the choice and combination of several versions of the coalescing media. The size of the media's granular structure can be changed to vary the porosity characteristics and finally the compressibility factor is governed by the density in which the media is packed into the element's housing.

While the standard manufactured element can be applied to most produced water processes, the permeability, porosity and compressibility factor can be influenced to provide a unique solution to applications with very unique oil droplet characteristics such as "low oil drop per volume" ratios, complex reverse emulsions and oil droplets coated with chemical surfactants.

The following diagrams will assist in describing how the dispersed oily water is treated and how the coalescing elements address the unique oil droplet characteristics often found in upstream applications.


Fig. 8 – Adsorption Process

The hydrocarbon contaminated produced water is channeled through the inner core of the continuous coalescing element (CCE). The top of the inner core is capped to force the flow of the oily water through the element. The thermoset polymeric backbone material media is designed to provide a micro-rugged contact surface area that allows for the increase in frictional forces between the dispersed oil droplets and the media. This effect, accompanied by the interfacial tension forces between the oil and the media, break up stable oil droplets 2 microns and larger and adsorbs them on to the media.

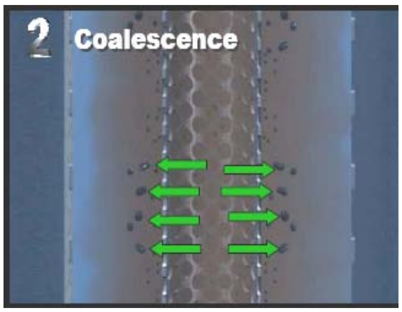


Fig. 9 - Coalescence

The media structure in the coalescing elements defines a non-linear migration path for the oil film in a radial outward direction. The media porosity and oil film migration path optimizes the impact probability of oil droplets. Therefore produced water with low oil drop counts per volume is funnelled into a confined area and impact probability is increased. Control of the above parameters varies the probability of impact of smaller oil droplet sizes. Flow velocity controls droplet impact, adsorption and coalescence rates of the media in the coalescing elements.

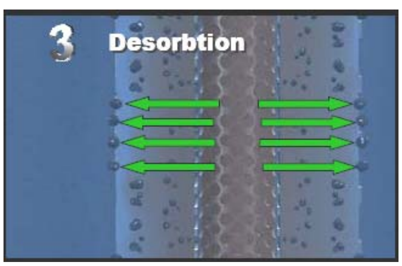


Fig. 10 - Desorbtion

The elasticity of the media structure in the coalescer element, along with the flow distribution and increased flow velocity of the water through the element, creates an inertial force and pressure drop that allows for the release of large oil droplets through the outer perimeter of the element.

The process of adsorption, coalescence and desorbtion repeats itself many times even when the element is fully saturated with oil. The continuous coalescing element cleans itself of the hydrocarbons through the desorbtion of the large oil globules which then possess a high rise velocity. These large oil globules are recovered in the gravity separation recovery system at the top of the vessel. This process of adsorption, coalescence, desorbtion and gravity separation enables the recovery of hydrocarbons on a continuous basis with minimum intervention.

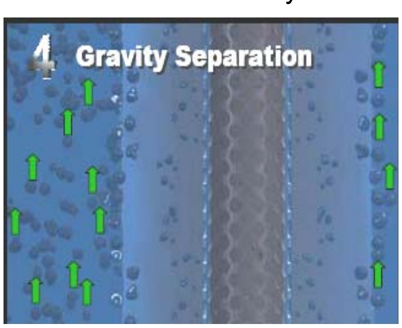


Fig. 11 – Gravity Separation

# 5 FIELD RESULTS

## 5.1 Field Apparatus

The field trial unit utilized for the Middle East site consisted of a three-stage 10 bar pressure rated system. Vessel body material is of stainless steel and each vessel incorporates a standard continuous coalescing element. The unit had a nominal flow rate capacity of 500 BWPD and maximum operating pressure and temperature of 10 barg and 95ºC respectively. A twin-set of bag filters (5 micron filters) was installed upstream of the Technology's system to capture any solid particle upsets in the process fluid. Four sample points on the unit allowed for sampling at the inlet of the bag filters, inlet of the first, second and third stages.

Fig. 12. – Field Apparatus

## 5.2 Sampling and Analysis

Sampling was done using 100 ml sample containers. Analysis was done with solvent extraction using Xylene as the solvent. Samples were measured using the Hach DR/4000u ultra-violet spectrum analyzer calibrated using crude oil produced from the wells feeding the facility.

One measurement method used to evaluate the performance of the process is the Video Imaging Process Analyzer (ViPA). This combines a high-resolution video microscope with an image analysis system. It captures images of the particles in a process flow and allows the monitoring and analysis of those particles in real time. Information on the shape, size, optical density and fourteen other parameters are recorded for each particle in the image before the data is saved and the next image is captured. Up to eight particle types – or sub-populations – can be stored. Approximately fifteen images are analyzed each second.

Oil in water emulsions - as all liquid in liquid emulsions - is characterized by their almost perfectly spherical shape. In sharp contrast, sand particles are crystalline and therefore very different in shape to the oil droplets. The analyzer can differentiate such geometries and organize them in a database.

This measuring device can plot recorded parameters as an overall distribution for each or all sub-populations. The graphs are reported on screen and on the optional 4-20 mA output. The analyzer is also equipped with a comprehensive suite of trend analysis software. It determines the trends and trigger alarms. This provides vital time, especially on the field, before a process goes out of specifications, to take corrective action and prevent process upsets. [3]

### 5.3 Production Station Middle East Offshore Facility

The Middle East offshore facility processed fluids from over 40 wells and is currently producing 90,000 – 160,000 BPD of fluids with a water cut of 53 – 60%. The crude oil has a 36.4 APIº Gravity and a viscosity of 4.73 cSt @ 40 degrees Celsius.

The Technology was trialed at the offshore facility to evaluate the performance of the system in de-oiling produced water at that station in several locations as shown namely:

- Downstream of Degassing Vessel V-5353
- Downstream of Test Hydrocyclone S-5333
- Downstream of Test Separator V-5307
- Downstream of Bulk Separator V-5356.

The produced water to be treated was varied based on feed location, operating pressure, and the selection of the online producing wells. The objective of the trial was to reduce the oil-in-water (OIW) as much as possible with a target of 20 mg/L suitable for re-injection and overboard discharge. Online analysis of the oil droplet size distribution of the produced water was performed at the following locations in the produced water stream:

- Downstream all three stages of the Technology process during all tests at all locations
- Downstream of Degassing Vessel V-5353
- Inlet and Outlet of Test Hydrocyclone S-5333
- Inlet and Outlet of Hydrocyclone S-5330
- Inlet and Outlet of Hydrocyclone S-5334
- Inlet and Outlet of Hydrocyclone S-5335
- Downstream of the Test Separator V-5307
- Downstream of the Bulk Separator V-5356.

The objective of this analysis was to be able to characterize the produced water quality through measurement of and determine the most optimum solution for de-oiling this water using the Technology. Well fluids enter three three-phase HP separators where oil, water and gas are separated. Produced water continues through corresponding hydrocyclones to degassing vessel V-5353. Separated oil continues to two MP separators where remaining water is separated from oil. Produced water goes through corresponding hydrocyclones before entering degassing vessel. Altogether degassing vessel receives feed from five hydrocyclones. In addition, there is a test separator and test hydrocyclone for well testing. The trial was conducted over a period of 14 days with 12 full running days (24hrs/day). The trial consisted of five parts:

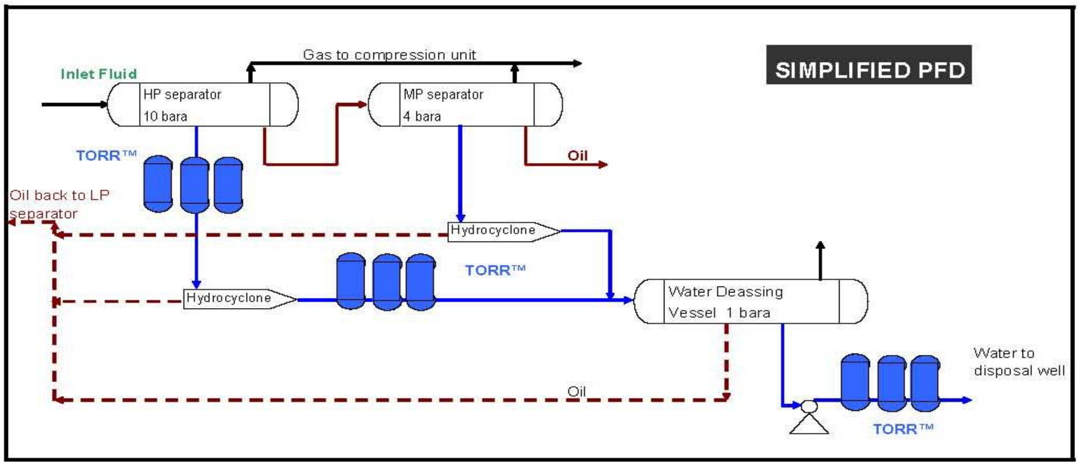

Fig. 13. – Simplified PFD

- #1 - Technology unit inlet was connected downstream of formation water disposal pumps P-537A to de-oil the water downstream the Degassing Vessel V-5353.
- #2 - Technology unit inlet was connected downstream of the test hydrocyclone S-5333 and BH 10-well was selected and connected (alone) to the test separator V-5307. Test separator was operated at 10 bar pressure.
- #3 - Continued as in above with the operating pressure in the test separator lowered to 5 bars.
- #4 - Technology unit inlet was connected downstream of the test separator (V-5307) and the pressure in the separator was raised to 10 bars. BH-10 was still the only well coming to the test separator.
- #5 - TORR™ unit inlet was connected downstream of the bulk separator (V-5356).

## 5.4 Results

**Table 1 – Sample Bottle Oil Concentration Mean Averages Taken by Site Operations**

| Trial Part | Inlet (Mean) | Stage 1 (Mean) | Stage 2 (Mean) | Outlet (Mean) |
|---|---|---|---|---|
| #1 | 141 ppm | 11 ppm | 5 ppm | 5 ppm |
| #2 | 1,123 ppm | 13 ppm | 7 ppm | 5 ppm |
| #3 | 942 ppm | 23 ppm | 11 ppm | 6 ppm |
| #4 | 1,908 ppm | 22 ppm | 11 ppm | 9 ppm |
| #5 | 1,937 ppm | 19 ppm | 13 ppm | 7 ppm |

**Table 2 - Oil Droplet Size Distribution ViPA Statistics (Inlet of Technology)**

| Inlet | Count | | | Volume | | |
|---|---|---|---|---|---|---|
| | d10 | d50 | d90 | d10 | d50 | d90 |
| #1 | 0.9 | 4.4 | 8.2 | 4.7 | 8.3 | 13.3 |
| #2 | 0.9 | 5.3 | 12.3 | 10.8 | 32.7 | 65.7 |
| #3 | 0.9 | 5.6 | 16.1 | 11.6 | 25.8 | 47.1 |
| #4 | 0.9 | 6.0 | 15.5 | 11.4 | 26.2 | 69.3 |
| #5 | 0.9 | 5.3 | 15.6 | 12.9 | 30.3 | 68.7 |

For the first trial part #1, inlet OIW concentration to the Technology system ranged between 113 and 180 mg/L whereas the outlet OIW concentration was consistently between 4 and 6 mg/L. For trial part #2, inlet OIW concentration to the technology system ranged between 900 and 1300 mg/L whereas the outlet concentration was consistently between 4 and 6 mg/L. On trial part #3, inlet OIW concentration ranged between 800 and 1,300 whereas the outlet OIW concentration was consistently between 4 and 8 ppm. Inlet OIW concentration ranged between 1800 and 2100 whereas the outlet OIW concentration was consistently between 6 and 15 ppm on trial part #4. And finally, the inlet OIW concentration ranged between 1,800 and 2,600 whereas the outlet OIW concentration was consistently between 6 and 9 ppm for trial part #5.

**Table 3 - Oil Droplet Size Distribution ViPA Statistics (Outlet of Technology)**

| Outlet | Count | | | Volume | | |
|---|---|---|---|---|---|---|
| | d10 | d50 | d90 | d10 | d50 | d90 |
| #1 | 1.6 | 4.2 | 10.6 | 6.7 | 14.8 | 23.3 |
| #2 | 1.7 | 9.1 | 23.2 | 15.1 | 25.1 | 30.3 |
| #3 | 1.6 | 6.5 | 15.3 | 11.2 | 22.8 | 28.3 |
| #4 | 1.2 | 5.6 | 19.5 | 13.6 | 21.6 | 28.6 |
| #5 | 1.4 | 4.9 | 14.3 | 11.0 | 23.6 | 28.5 |

For trial part #1, the Technology unit was very successful in reducing the OIW concentration of free and dispersed oil in the commingled produced water from 100 – 200 ppm down to 5 ppm. Most of the dispersed oil droplets (contributing to volume) are in the range of 4-13 microns.

The Technology also performed well with BH-10, downstream of both the test hydrocyclone and the test separator. Most of the time the outlet OIW concentration was below 10 ppm, however, more stages were needed to reach the low OIW concentration target when the inlet concentration was high (800-2000 ppm). Most of the dispersed oil droplets (contributing to volume) were in the range of 11-65 microns.

The performance of the Technology downstream of the bulk separator V-5356 was also good. The outlet concentration was below 10 ppm regardless of high inlet concentrations (1800-2600 ppm). Most of the dispersed oil droplets (contributing to volume) are in the range of 13-69 microns.

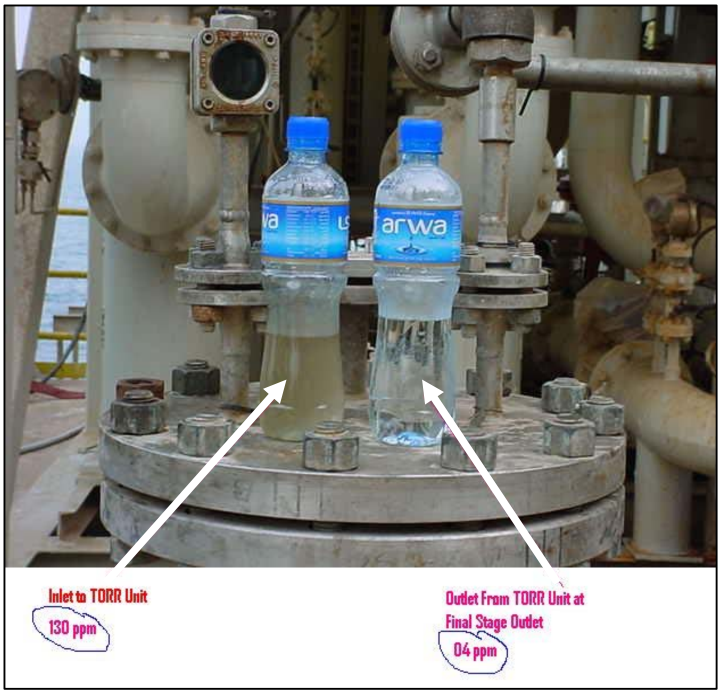


Fig. 14. – Visual Samples

Overall, more than 97% of the OIW was removed from the produced water at all trial locations and the target of 20 mg/L OIW in the effluent was attained and maintained throughout the trial.

## 6 CONCLUSIONS

Analysis of the findings and results above renders the following conclusions:

1- The Technology was very successful in reducing the OIW concentration of free and dispersed oil in the commingled produced water from 100 – 200 ppm down to 5 ppm. Most of the time first stage was already reducing the OIW concentration below 10 ppm. Most of the dispersed oil droplets (contributing to volume) are in the range of 4-13 microns.

2- The Technology also performed well with BH-10, downstream of both the test hydrocyclone and the test separator. Most of the time the outlet OIW concentration was below 10 ppm, however, more stages were needed to reach the low OIW concentration target when the inlet concentration was high (800-2000 ppm). Most of the dispersed oil droplets (contributing to volume) were in the range of 11-65 microns.

3- The performance of the Technology downstream of the bulk separator V-5356 was also good. The outlet concentration was below 10 ppm regardless of high inlet concentrations (1800-2600 ppm). Most of the dispersed oil droplets (contributing to volume) are in the range of 13-69 microns.

4- Overall, more than 97% of the OIW was removed from the produced water at all trial locations and the target of 20 mg/L OIW in the effluent was attained and maintained throughout the trial.

5- The Technology has removed and recovered dispersed oil droplets having diameters 2 microns and larger from produced water.

## 7 REFERENCES

[1] RPA® Liquid Sorbent, Canada Patent 2,085,951.

[2] TORR™ Patent Pending, Canada PCT/CA01/-1284, UK 0022013.7

[3] R. GASKIN. The ViPA, Jorin Limited, http://www.jorin.co.uk/vipa.htm.